(12) UK Patent Application (19) GB (11) 2 030 169 A

(21) Application No 7932096
(22) Date of filing 17 Sep 1979
(23) Claims filed 17 Sep 1979
(30) Priority data
(31) 9774/78
(32) 19 Sep 1978
(33) Switzerland (CH)
(43) Application published
2 Apr 1980
(51) INT CL³
C09B 29/08
C09B 31/043
D06P 1/16
(52) Domestic classification
C4P 122 126 130 1A1B2
1D1 1F2 1F5 1F6 1H2 1H4
2G2AY 2H3 2H7 2H8 M
(56) Documents cited
GB 1227871
(58) Field of search
C4P
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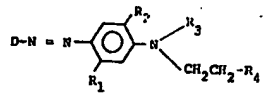
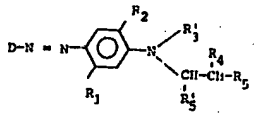
(54) **Improvements in or relating to organic compounds**

(57) The present invention relates to a mixture of disperse dyestuffs containing at least one compound of formula I,



I

and at least one compound of formula II



II

in which D, is a disperse dye diazo component radical,

R_1, is hydrogen, alkyl, alkoxy or acylamino,

R_2, is hydrogen, alkyl or alkoxy which is optionally substituted,

R_3, is hydrogen, alkenyl, chloro- or bromo-alkenyl, linear alkyl which is optionally substituted,

R_3', is hydrogen, alkenyl, chloro- or bromo alkenyl, linear or branched alkyl, which is optionally substituted,

R_4, is a sulphur-free acyloxy or alkoxy-carbonyl radical,

one of R_5 and R_5' is hydrogen and the other is methyl,

the D's R_1's, R_2's and R_4's being identical, which mixture contains 15 to 85% compound of formula I and 85 to 15% compound of formula II, and has good dispersion stability and is useful for dyeing disperse dye dyeable substrats with good build-up power and gives dyeings have good wet-fastness.

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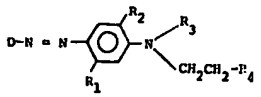
SPECIFICATION

Improvements in or relating to organic compounds

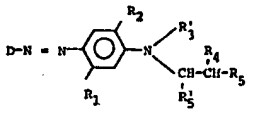
The present invention relates to mixtures of disperse dyestuffs which mixtures possess improved properties over the individual dyestuffs.

More particularly, the present invention provides a mixture of disperse dyestuffs containing at least one compound of formula I,



I

and at least one compound of formula II



II

in which D, is a disperse dye diazo component radical,

R_1, is hydrogen, alkyl, alkoxy or acylamino,

R_2, is hydrogen, alkyl or alkoxy which is optionally mono-substituted by a substituent selected from halogen, cyano, acyl, acyloxy, hydroxyl, alkoxy, phenyl and phenoxy,

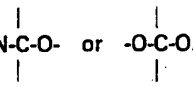
R_3, is hydrogen, alkenyl, chloro- or bromo-alkenyl, linear alkyl which is optionally substituted by up to two substituents selected from halogen, acyloxy, hydroxyl, and alkoxy or mono-substituted by a cyano, acyl, phenyl or phenoxy group,

R_3', is hydrogen, alkenyl, chloro- or bromo alkenyl, linear or branched alkyl, which is optionally substituted by up to two substituents selected from halogen, acyloxy, hydroxyl, and alkoxy or mono-substituted by a cyano, acyl, phenyl or phenoxy group,

R_4, is a sulphur-free acyloxy or alkoxy-carbonyl radical,

one of R_5 is R_5' is hydrogen and the other is methyl, the D's, R_1's, R_2's and R_4's being identical, any alkyl groups or moieties and any alkoxy groups in such dyestuffs contain 1 to 8 carbon atoms, any alkenyl groups 2 to 4 carbon atoms, and said mixture contains 15 to 85% compound of formula I and 85 to 15% compound of formula II.

It will be appreciated that the compounds of formula I and formula II are free from acetal groupings i.e.



By halogen is meant chlorine, bromine or iodine.

The preferred halogens are chlorine and bromine.

By 'acyl' is meant groups of formula R-Y- and R'-Z wherein R is a alkyl, alkenyl, C_{5-7} cycloalkyl, phenyl or a heterocyclic group, (preferably alkyl, alkenyl (C_{5-7}) cycloalkyl or phenyl), which alkyl is optionally mono-substituted by halogen, hydroxy, (C_{1-2}) alkoxy, phenyl or phenoxy and which phenyl is optionally substituted by up to two substituents selected from halogen, (C_{1-2}) alkyl and (C_{1-2}) alkoxy,

Y is -O-CO-, or - OSO_2-(-O-bound to R)or - SO_2 -

R ' is hydrogen or has one of the significances of R,

Z is -CO-, -NR"CO- or -NR"SO_2- (-N bound to R'), and

R" is hydrogen or has one of the significance of R

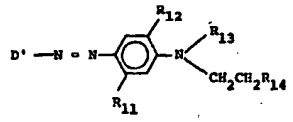
and acyloxy and acylamino are to be understood accordingly.

When the alkyl and/or alkoxy groups in the dyestuffs are substituted they are preferably monosubstituted or are substituted by a hydroxyl group and a further substituent. Preferably the alkyl and alkoxy radicals contain 1 to 4, more preferably 1 or 2 carbon atoms. Preferred alkenyl groups contain 3 carbon atoms. The preferred cycloalkyl is cyclohexyl.

Preferred diazo component radicals ar th se of the benzene seri s (opti nally disaz c mponent radicals) and diaz component radicals of the benz thiazolyl, thi phene r thiazolyl s ries.

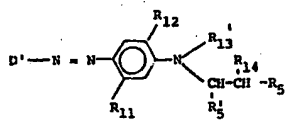
More preferably, D is thi phene-2 substitut d by up t two nitr groups; benzothiazolyl-2 in which the benzene nucleus is substituted by up t tw substituents selected from chl rine and nitr ; r phenyl substituted in the para positi n by nitr , alkylsulph nyl, aminosulphonyl, mono- or dialkylaminosulphonyl r phenylazo (in which the benzene nucleus is optionally substituted by up to three substitu nts select d fr m methyl, methoxy, chlorine, bromine and nitr) and opti nally bearing up t tw further substituents selected fr m halogen, nitro, cyano or alkylsulphonyl.

Representative mixtures are those containing at least one compound of formula Ia



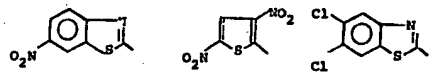
Ia

and at least one compound of formula IIa

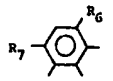


IIa

in which D' is a radical of formula (a), (b), (c) or (d)



(a) (b) (c)



(d)

wherein R_6 is hydrogen, chlorine, bromine, iodine, nitro or cyano,

R_7 is nitro, (C_{1-2})alkylsulphonyl, amino-sulphonyl, mono- or di(C_{1-2}) alkylamino-sulphonyl or phenylazo in which the benzene ring is optionally substituted by up to three substituents selected from methyl, methoxy, chlorine, bromine and nitro,

R_8 is hydrogen, chlorine or bromine,

R_9 is hydrogen, chlorine, bromine, iodine, cyano or (C_{1-2}) alkylsulphonyl, with the proviso that one of R_8 and R_9 is hydrogen,

R_{11} is hydrogen, methyl, methoxy, ethoxy, formylamino, alkyl (C_{1-4}) carbonylamino, alkyl (C_{1-2}) carbonylamino monosubstituted by hydroxyl, chlorine, bromine, cyano, phenyl, (C_{1-3}) alkoxy or phenoxy, alkoxy-(C_{1-4}) carbonylamino, ethoxycarbonylamino monosubstituted by hydroxy, (C_1d2-$_3$) alkoxy or (C_{1-2}) alkoxyethoxy, benzoylamino or (C_{1-2}) alkylsulphonylamino,

R_{12} is hydrogen, methyl, (C_{1-2}) alkoxy, (C_{1-2})-alkoxyethoxy or (C_{1-2}) alkoxy monosubstituted by chlorine, bromine, cyano or phenyl,

R_{13} is hydrogen, linear (C_{1-4}) alkyl, (C_{2-3})- alkenyl, linear (C_{2-3}) alkyl mono-substituted by (C_{1-2}) alkoxy, cyano, formyloxy, alkyl (C_{1-4}) carbonyloxy, alkoxy (C_{1-3}) carboyl, benzoyloxy or alkoxy (C_{1-3}) carbonyloxy,

R'_{13} has one of the significances of R_{13} but where the alkyl and substituted alkyl radicals are linear or branched,

R_{14} is formyloxy, alkyl (C_{1-4}) carbonyloxy, benzoyloxy, phenoxyacetoxy, alkoxy (C_{1-4})- carbonyloxy, alkoxy (C_{1-4}) carbonyl, alkoxy (C_{1-2}) ethoxycarbonyl, alkoxy (C_{1-2}) ethoxycarbonyloxy, alkoxy (C_{1-2}) alkyl (C_{1-2}) carbonyloxy, mono- or di (C_{1-4}) alkyl) aminocarbonyloxy or phenylaminocarbonyloxy wherein the benzene nucleus is optionally substituted by up to two substituents selected from chlorine, bromine, methyl and methoxy,

whereby in such mixture D', R_{11}, R_{12}, and R_{14} in the compound of formula Ia is identical with that of the compound of formula IIa.

More preferred mixtures are those wherein D' is a group of formula (d), especially those wherein R_6 is R'_6, where R'_6 is hydrogen, chlorine, bromine or nitro, R_7 is nitro, R_8 is hydrogen and R_9 is R'_9 where R'_9 is hydrogen, chlorine, bromine, ,cyano or methylsulphonyl.

Even more preferred mixtures are those wherein D' is a group of formula (d) wherein R_6 is R'_6, R_7 is nitro R_8 is hydrogen, R_9 is R'_9, R_{11} is R'_{11} where R'_{11} is hydrogen, methyl, alkyl (C_{1-2}) carbonylamin , chloro- or bromoalkyl-(C_{1-2}) carbonylamin , alkoxy (C_{1-2}) carbonylamin r alk xy-(C_{1-2}) eth xycarbonylamino, R_{12} is R'_{12}, wh r R'_{12} is hydrogen, methoxy or eth xy, R_{13} is R_{13a}, wh rein R_{13a} is lin ar (C_{2-3}) alkyl, allyl or lin ar (C_{2-3}) alkyl monosubstituted by cyan , alkyl (C_{1-2}) carbonyloxy, alk xy (C_{1-2})- carb nyl or alkoxy (C_{1-2}) carbonyl xy, R'_{13} has n of the significances of R_{13a} but where the pti nally substituted (C_{2-3}) alkyl may be lin ar or branched and R_{14} is alkyl-(C_{1-2}) carbonyloxy or alkoxy (C_{1-2}) carbonyl xy.

Th preferred coupling c mp nent in th mixtures of the invention are those where R'_5 is hydrog n, R_5 is methyl, R_1 is R_{11}, R_2 is R_{12}, R_3 is R_{13}, R'_3 is R'_{13} and R_4 is acyl xy specially alkyl (C_{1-2}) carb nyloxy or

alkoxy-(C_{1-2}) carbonyloxy, especially those wherein R_{11} is R'_{11}, R_{12} is R'_{12}, R_{13} is R_{13a} and R'_{13} has one of the significances R_{13a} but wher the optionally substituted alkyl may be linear or branched.

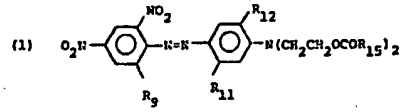
The following mixtures of the compounds of formula Ia and IIa are most preferred

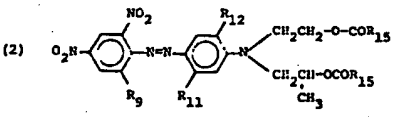
(i) those where D' is a radical (d) wherein R_6 is chlorine or bromine, especially chlorine, R_7 is nitro, R_8, R_9, R_{11} and R_{12} are hydrogen, R_{13} and R'_{13} are cyanoethyl, R_{14} is alkyl (C_{1-2}) carbonyloxy, especially acetoxy, R_5 is methyl and R'_5 is hydrogen;

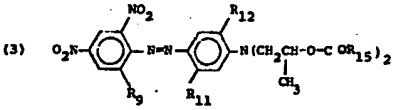
(ii) those where D' is a radical (d) wherein R_6, R_8, R_{11} and R_{12} are hydrogen, R_7 is nitro, R_9 is cyano, R_{13} and R'_{13} are cyanoethyl, R_{14} is alkyl (C_{1-2}) carbonyloxy, especially acetoxy, R_5 is methyl and R'_5 is hydrogen;

(iii) those wherein D' is a radical (d) wherein R_6 and R_9, independently, are chlorine, or bromine, especially chlorine, R_7 is nitro, R_8, R_{11} and R_{12} are hydrogen, R_{13} and R'_{13} are cyanoethyl, R_{14} is alkyl (C_{1-2}) - carbonyloxy, especially acetoxy, R_5 is methyl and R'_5 is hydrogen;

(iv) a mixture of the following three dyes:

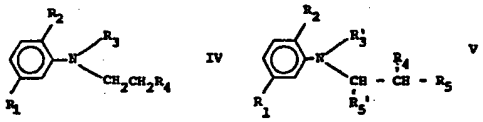






in which each R_9 is chlorine, bromine or iodine, especially bromine, each R_{11} is alkyl (C_{1-2})-carbonylamino, especially acetylamino, each R_{12} is (C_{1-2}) alkoxy, especially ethoxy and each R_{15} is (C_{1-2}) alkyl, especially methyl, especially a mixture containing approximately 25% (i) 50% (2) and 25% (3).

The preferred method of preparing the mixtures according to the invention is to couple a diazotised amine with a mixture containing at least one compound of formula IV and at least one compound of formula V,



whereby at least 15 mol % of a compound of formula IV and at least 15 mol % of a compound of formula V is present.

Diazotization and coupling are carried out in accordance with known methods.

It will also be appreciated that the mixtures of the invention may also be obtained by admixing dyes of formula I and II together, preferably at the time of making the dyeing preparation.

The dyestuff mixtures according to the present invention are made up into dyeing preparations by known methods, for example by grinding in the presence of disperse agents and/or fillers, followed by drying. It will be appreciated that when the mixtures are obtained by admixing dyes of formula I and II, the dyeing preparation can be made by admixing the already ground dyes of formula I and II or by grinding the already mixed dyes of formula I and II.

The dyestuff preparations containing the mixtures according to the present invention are useful for dyeing or printing textiles comprising or consisting of synthetic, semi-synthetic, hydrophobic, high-molecular weight organic substrates from aqueous suspensions. Preferred substrates are textiles of linear, aromatic polyesters, cellulose $2^1/2$ acetate, cellulose triacetate and synthetic polyamides. Dyeing, padding or printing may be carried out in accordance with known methods, for example as described in French Patent No. 1,445,371.

It is known that some disperse dyes exist in the thermoinstable form which causes problems in that they do not build-up int the fibre which leads to uneven dyeings having poor rubbing and wash fastness and which caus s special difficulties for cross-wound sp ol dyeing. Such dyestuffs can b converted to the therm stable f rm by h at-treatment. H w ver with the dyestuff preparati ns made with some of th mixtures according t the present inv ntion the ab ve-menti ned disadvantages do not occur and thus, the further conversion e.g. heat-treatment step is unnecessary.

Further, the mixtures of th inv nti n have go d disp rsion stability, hav good build-up power and give dyeings with go d rubbing- w t-fastn sses.

The foll wing Examples furth r serve to illustrate the inv ntion. In the Examples all parts are by w ight, unless otherwise stated, and all temp ratures ar in degree centigrade.

Example 1

17.3 Parts 2-chl ro-4-nitr anilin are stirred overnight in a mixture of 44 parts conc. hydrochloric acid and 100 parts water. 60 Parts ice are added thereto and a solution of 6.9 sodium nitrite in 25 parts water are added dropwise over a period of 30 minutes at 0 - 3°. After 2½ hours when diazotization is completed some undissolved product is filtered off and a mixture of 11.6 parts N-(2'-acetoxyethyl)-N-(2'-cyanoethyl)-aminobenzene, 12.3 parts N-(2'acetoxypropyl)-N-(2'-cyanoethyl)-aminobenzene and 20 parts acetic acid are added dropwise over a period of 45 minutes at 0 to 3° to the clear diazonium salt solution. The coupling reaction is completed by the addition of 50 parts sodium acetate. The precipitated dyestuff mixture is filtered, washed with 4000 parts water and dried.

The dyestuff mixture without conversion to the thermostable form may be up into a dyeing preparation in accordance with known methods with the addition of a dispersing agent, e.g. a commercially available ligninsulphonate which preparation has good dispersion stability.

Example 2

16.3 parts 2-cyano-4-nitroaniline are added at 5 to 10° to 100 parts (95%) sulphuric acid. At the same temperature, 32 parts (40%) nitrosylsulphuric are added dropwise and the whole is stirred for 3 hours. The so obtained diazonium salt solution is poured onto a mixture of 300 parts ice and 100 parts water. Some undissolved product is filtered off and a mixture of 11.6 parts N-(2'-acetoxyethyl)-N-(2'cyanoethyl)-aminobenzene, 12.3 parts N-(2'-acetoxypropyl)-N-(2'-cyanoethyl)-aminobenzene and 30 parts acetic acid is added dropwise at 0 to 3° to the clear solution. After 3 hours the precipitated dyestuff mixture is filtered, washed free of acid and dried. Dyestuff preparations made therefrom without conversion have good dispersion stability.

Example 3

A mixture of 16.2 parts N-(2'acetoxyethyl)-N-(2'-cyanoethyl)aminobenzene, 7.4 parts N-(2'-acetoxypropyl)-N-(2'-cyanoethyl)amino benzene and 30 parts acetic acid are added dropwise to the clear diazonium salt solution obtained as described in Example 2 at 0 to 3°. The precipitated dyestuff mixture is filtered and washed free from acid. The presscake is subsequently stirred in 300 parts water. The homogenous suspension is put in a steel autoclave and is stirred for 3 hours at 105 - 110°. After cooling and filtering, a thermostable dyestuff mixture is obtained which may be made up into useful dyestuff preparations.

Example 4

13.8 Parts 4-nitroaniline are dissolved in 80 parts water at 70 - 80° with the addition of 28 parts conc. hydrochloric acid. The solution is cooled to 0 to 2° by adding 200 parts ice and diazotization is quickly carried out with a solution of 6.9 parts sodium nitrite in 14 parts water. Some solid product is filtered off and over a period of 60 minutes a mixture of 13.9 parts N-(2'-acetoxyethyl)-N-(2'-cyanoethyl)aminobenzene, 9.85 parts N-(2'-acetoxypropyl)-N-(2'cyanoethyl)aminobenzene and 20 parts acetic acid is added dropwise at 0 to 3° to the clear diazonium salt solution. After the addition of 40 parts sodium acetate coupling is complete and the precipitated dyestuff mixture is filtered, washed and dried. The mixture, without conversion, is made into a finely divided dyeing preparation with the addition of dispersing agent, which preparation gives orange dyeings on polyester fibres.

Example 5

At 0 to 3° a mixture of 18.6 parts N-(2'-acetoxy-ethyl)-N-(2'-cyanoethyl)aminobenzene, 4.9 parts N-(2'-acetoxypropyl)-N-(2'-cyanoethyl)aminobenzene and 20 parts acetic acid are added dropwise over a period of 45 minutes to the diazonium-salt solution prepared as described in Example 1. 50 Parts sodium acetate are added to complete the coupling reaction. The precipitated dye mixture is filtered, washed with 4000 parts water and dried in vacuo for at least 48 hours at 100-105°.

After heat treatment to convert the mixture to the thermostable form the dye mixture is made up into an excellent finely dispersed dyestuff preparation.

Example 6

69 parts sodium nitrite are added portionwise to 1200 parts conc. sulphuric acid at 60-70° with energetic stirring. Stirring is continued for a further 10 minutes and the mixture is cooled to 30° whereupon 207 parts 2,6-dichloro-4-nitroaniline are added. Diazotization is complete after 3 hours. The yellow-brown solution is poured onto a mixture of 3400 ice and 2500 parts water. A mixture of 116 parts N-(2'-acetoxyethyl)-N-(2'-cyanoethyl)aminobenzene, 123 parts N-(2'-acetoxypropyl)-N-(2'-cyanoethyl)amin benzen and 200 parts acetic acid ar added dr pwise with stirring at 0 to 5° t th btained aqueous diazonium-salt solution. The precipitated dy mixture is filtered, washed acid-free, dried and, without conversi n t the therm stabl forms is mad up in accordance with kn wn meth ds, with the addition of a ligninsulphonate into a fine dispersion. The preparation has very good dispersi n stability combined with go d build-up power on polyester material.

Example 7

A mixtur f 46 parts N-(2'-ac toxyethyl)-N-(2'-cyanoethyl)amin benzene, 197 parts N-(2'-acetoxypropyl)-

N-(2'-cyan ethyl)amin benz ne and 200 parts acetic acid are dropped into the diaz nium salt solution of Example 6 at 0 t 5°. Th precipitated dye is filtered and washed acid fre . A dispersion stable dye mixture is obtained which gives satisfactory dyeings without conversion to the thermostable form.

Example 8

600 Parts water and 194 parts 1-acetylamino-4-ethoxy-3-amino benzene are put in an autoclave which is rendered oxygen free by pasing nitrogen therethrough. The whole is heated to 55° and the amine is reacted for 2 hours with a mixture consisting of 52.8 parts ethyleneoxide and 69.6 parts propylene oxide whereupon the temperature rises to 62°. The mixture is stirred for 6 hours at 60° and then cooled to 5°. Excess ethylene- and propyleneoxide are removed by means of a water jet pump and then passing nitrogen therethrough. The autoclave is opened and the crystalline precipitated product is filtered, washed with a little cold water and dried in vacuo at 60°.

148 Parts of the dried product are dissolved in 150 parts glacial acetic acid. At 80-90° over a period of 1 hour 122 parts acetic acid anhydride are added dropwise. The mixture is then heated to 110° and stirred for 3 hours at this temperature until there are no more traces of nonesterified material (tested by thin layer chromatography). The mixture of coupling components is cooled to room temperature.

With energetic stirring 31.1 parts sodium nitrite are added at 60 to 70 to 540 parts conc. sulphuric acid. Stirring is continued for a further 10 minutes at 60°, the mixture cooled to 10° and 117.9 parts 2-bromo-4,6-dinitroaniline are added thereto. Diazotization is complete after 3 hours. The diazonium solution is added to a mixture of all the coupling component obtained above, 450 parts glacial acetic acid, 3000 parts ice and 9 parts aminosulphonic acid at −5 to +2° over a period of 30 to 40 minutes. The dyestuff precipitates quickly and the solution is stirred at 0 to 2°C until no further diazo compound is detectable. The dye suspension is adjusted to pH 6 to 7 by the addition of 30% sodium hydroxide solution. Then the solution is heated to 85° over a period of an hour and is kept at this temperature for an hour followed by heating to 90° and stirred for a further hour whereby the dyestuff components convert to the thermostable form. The dye is then filtered, washed with 5000 parts hot water and dried in vacuo at 80°.

D Preparation of Dispersion

In a flask, 78 parts of the dye mixture of Example 8 and 222 parts commercially available ligninsulphonate dispersing agent in 100 to 150 parts water are ground with 800 parts by volume silicia quartz beads for 6 hours (2000-2500 R.p.m.). The whole is diluted with 300 parts water and suction filtered. Any dyestuff and/or dispersing agent remaining on the beads is rinsed into the flask with a little water. The dispersion is adjusted to pH 6 to 6.5 with phosphoric acid and spray-dried (hot air 130°).

Example 9

Preparation of Dye A

232 Parts N-(2'-acetoxyethyl)-N-(2'-cyanoethyl)-aminobenzene and 200 parts acetic acid were poured into the diazonium salt solution produced as described in Example 6 at 0 to 5°. The precipitated dye is filtered washed free of acid and dried.

Preparation of Dye B

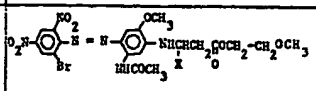
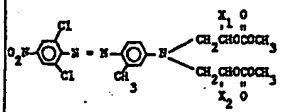
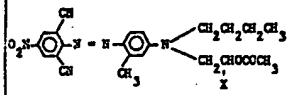
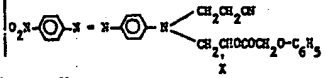
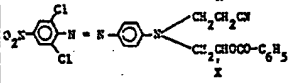
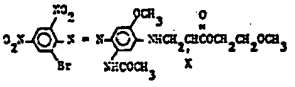
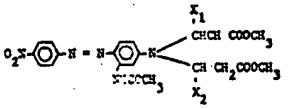
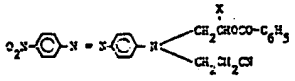
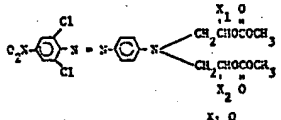
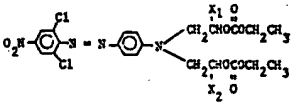
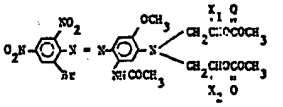
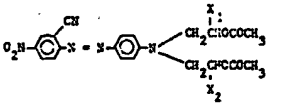
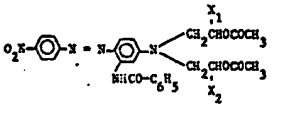
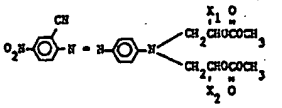
The diazonium salt solution of Example 6 is coupled with 246 parts N-(2'-acetoxypropyl)-N-(2'-cyanoethyl)aminobenzene in 200 parts acetic acid. The dye is filtered, washed and dried.

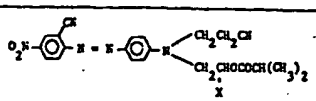
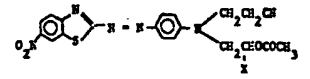
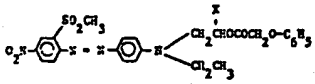
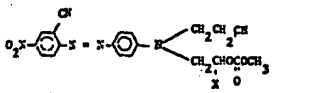
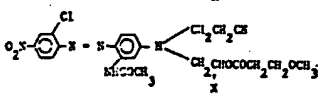
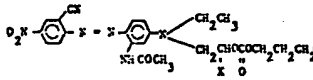
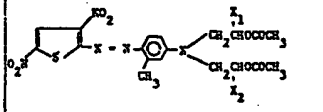
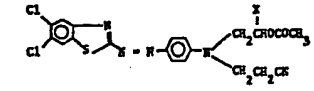
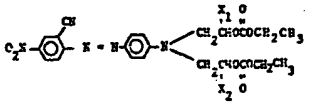
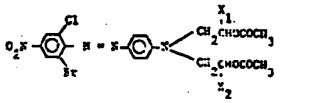
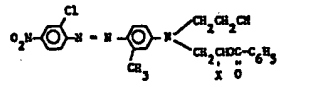
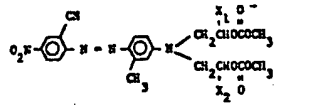
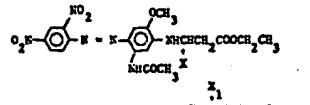
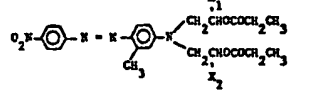
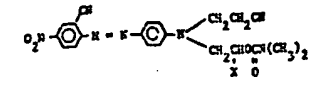
Preparation of Dyeing Formulation

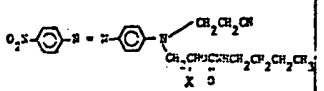
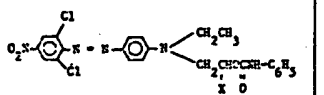
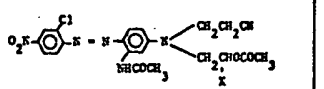
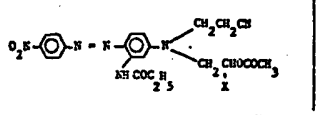
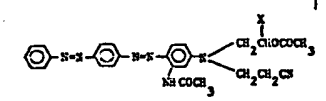
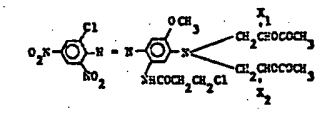
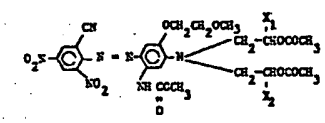
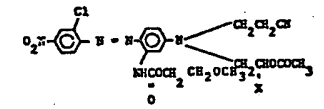
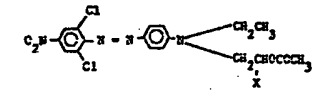
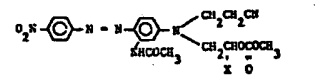
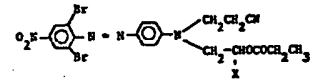
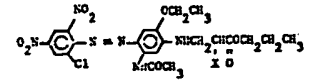
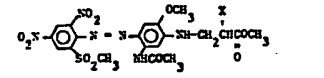
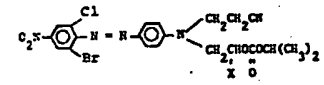
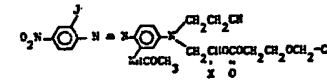
22.2 Parts dye A and 70.8 parts dye B are ground and dried with 207 ligninsulphonate as described above under D. The powdered product obtained has notable dispersion stability.

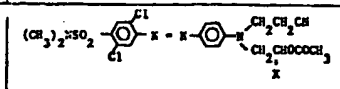
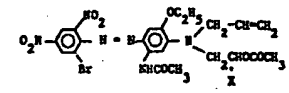
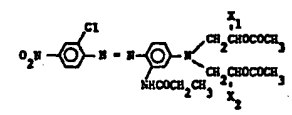
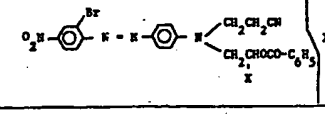
The mixtures given in the following Table may be prepared in accordance with the procedures of the foregoing Examples.

TABLE

Ex. No.	General Formula	1st Component	Mol %	2nd Component	Mol %	3rd Component	Mol %	shade on Polyester
10		X = H	50	X = CH_3	50		-	navy-blue
11		X_1 = H X_2 = H	ca.25	X_1 = CH_3 X_2 = CH_3	ca. 25	X_1 = H X_2 = CH_3	ca. 50	brown
12		X = H	40	X = CH_3	60		-	blue
13		X = H	50	X = CH_3	50		-	orange
14		X = H	70	X = CH_3	30		-	yellow-brown
15		X = H	55	X = CH_3	45		-	navy-blue
16		X_1 = H X_2 = H	ca.25	X_1 = CH_3 X_2 = CH_3	ca.25	X_1 = CH_3 X_2 = H	ca.50	scarlet
17		X = H	50	X = CH_3	50			orange
18		X_1 = H X_2 = H	ca.25	X_1 = CH_3 X_2 = CH_3	ca.25	X_1 = H X_2 = CH_3	ca.50	yellow-brown
19		X_1 = H X_2 = H	ca.25	X_1 = CH_3 X_2 = CH_3	ca.25	X_1 = H X_2 = CH_3	ca.50	yellow-brown
20		X_1 = H X_2 = H	ca.25	X_1 = CH_3 X_2 = CH_3	ca.25	X_1 = H X_2 = CH_3	ca.50	navy-blue
21		X_1 = H X_2 = H	ca.25	X_1 = CH_3 X_2 = CH_3	ca.25	X_1 = H X_2 = CH_3	ca.50	red
22		X_1 = H X_2 = H	ca.25	X_1 = CH_3 X_2 = CH_3	ca.25	X_1 = H X_2 = CH_3	ca.50	scarlet
23		X_1 = H X_2 = H	ca.25	X_1 = CH_3 X_2 = CH_3	ca.25	X_1 = H X_2 = CH_3	ca.50	red

Ex. No.	General Formula	1st Component	Mol %	2nd Component	Mol %	3rd Component	Mol %	shade on Polyester
24		X = H	45	X = CH_3	55		-	red
25		X = H	50	X = CH_3	50		-	red
26		X = H	50	X = CH_3	50		-	ruby
27		X = H	30	X = CH_3	70		-	red
28		X = H	55	X = CH_3	45		-	red
29		X = H	50	X = CH_3	50		-	reddish violet
30		X_1 = H X_2 = H	ca.25	X_1 = CH_3 X_2 = CH_3	ca.25	X_1 = H X_2 = CH_3	ca.50	blue
31		X = H	50	X = CH_3	50		-	scarlet
32		X_1 = H X_2 = H	ca.25	X_1 = CH_3 X_2 = CH_3	ca.25	X_1 = H X_2 = CH_3	ca.50	red
33		X_1 = H X_2 = H	ca.25	X_1 = CH_3 X_2 = CH_3	ca.25	X_1 = H X_2 = CH_3	ca.50	yellow-brown
34		X = H	50	X = CH_3	50		-	red
35		X_1 = H X_2 = H	ca.25	X_1 = CH_3 X_2 = CH_3	ca.25	X_1 = H X_2 = CH_3	ca.50	ruby
36		X = H	50	X = CH_3	50		-	reddish navy-blue
37		X_1 = H X_2 = H	ca.25	X_1 = CH_3 X_2 = CH_3	ca.25	X_1 = H X_2 = CH_3	ca.50	scarlet
38		X = H	70	X = CH_3	30		-	red

Ex. No.	General Formula	1st Component	Mol %	2nd Component	Mol %	3rd Component	Mol %	shade on polyester
39		X = H	55	X = CH_3	45		–	orange
40		X = H	60	X = CH_3	40		–	brown
41		X = H	50	X = CH_3	50		–	red
42		X = H	25	X = CH_3	75		–	scarlet
43		X = H	50	X = CH_3	50		–	scarlet
44		X_1 = H X_2 = H	ca. 25	X_1 = CH_3 X_2 = CH_3	ca. 25	X_1 = H X_2 = CH_3	ca. 50	navy-blue
45		X_1 = H X_2 = H	ca. 25	X_1 = CH_3 X_2 = CH_3	ca. 25	X_1 = H X_2 = CH_3	ca. 50	brown
46		X = H	30	X = CH_3	70		–	red
47		X = H	85	X = CH_3	15		–	brown
48		X = H	20	X = CH_3	80		–	scarlet
49		X = H	65	X = CH_3	35		–	yellow-brown
50		X = H	35	X = CH_3	65		–	navy-blue
51		X = H	50	X = CH_3	50		–	navy-blue
52		X = H	15	X = CH_3	85		–	yellow-brown
53		X = H	80	X = CH_3	20		–	ruby

Ex. No.	General Formula	1st Component Mol %		2nd Component Mol %		3rd Component Mol %		shade on Polyester
54		X = H	60	X = CH_3	40		-	orange
55		X = H	50	X = CH_3	50		-	navy-blue
56		X_1 = H X_2 = H	ca.25	X_1 = CH_3 X_2 = CH_3	ca.25	X_1 = H X_2 = CH_3	ca.50	ruby
57		X = H	75	X = CH_3	25		-	scarlet

Application Example A

Dyeing Preparation II

93 Parts of Dyestuff A above are ground with 207 parts ligninsulphonate as described above under D.

Dyeing Preparation III

93 Parts dyestuff B above are ground with 207 parts ligninsulphonate as described above under D.

1000 Parts polyester material are pre-wetted for 5 minutes at 60° with 30 parts ammonium sulphate dissolved in 14 litres water and adjusted to pH5 with 85% formic acid. 31.6 Parts of dyeing preparation II and 8.4 parts dyeing preparation III dispersed in 1 litre water are added thereto. The dyebath is heated over 30 minutes to 130° and dyeing is conducted for 60 minutes. The dyebath is cooled to 80°, the dyed substrate removed, rinsed and dried. A even, rubbing-fast yellow-brown dyeing is obtained.

Application Example B

3 Parts of the preparation D above are stirred in 4000 parts water at 60°. With this dyebath 100 parts polyester fibre is dyed with the addition of 20 parts ortho-phenylphenol for 1 hour at 98°. After cooling, rinsing, soaping and drying a navy-blue dyeing with good fastnesses is obtained.

Application Example C

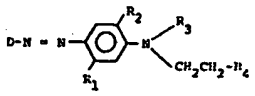
7 Parts of the mixture of Example 1 are ground to a fine powder with 4 parts sodiumdinaphthylmethane-sulphonate, 4 parts sodiumcetylsulphate and 5 parts anhydrous sodium sulphate in a ball mill for 48 hours.

1 Part of this dyeing preparation is pasted with a little water and the suspension is added to a dyebath containing 3 parts sodiumlaurylsulphate in 4000 parts water. 100 Parts scoured polyester (liquor to goods ratio 40:1) are added to the bath at 40 to 50°, 20 parts of a chlorobenzene are added, the bath is slowly heated to 100° and dyeing is carried out for 1 to 2 hours at 95-100°. The even red dyeing which is washed, soaped, washed again and dried has good fastnesses.

In analogy to the above procedures the dyestuff mixtures of Examples 2 to 57 may be used to dye polyester fibres.

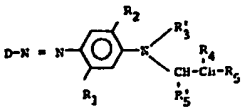
CLAIMS

1. A mixture of disperse dyestuffs containing at least one compound of formula I,



I

and at least one compound of formula II



II

in which

D, is a disperse dy diazo comp nent radical,

R_1, is hydrogen, alkyl, alk xy or acylamin ,

R_2, is hydrogen, alkyl or alkoxy which is opti nally mono-substituted by a substituent selected from halogen, cyan , acyl, acyl xy, hydroxyl, alkoxy, phenyl and phenoxy,

R_3, is hydrogen, alkenyl, chloro- or bromo-alkenyl, linear alkyl which is optionally substituted by up to two substituted selected from halogen, acyloxy, hydroxyl, and alkoxy or mono-substituted by a cyano, acyl, phenyl or phenoxy group,

R_3', is hydrogen, alkenyl, chloro- or bromo alkenyl, linear or branched alkyl, which is optionally substituted by up to two substituents selected from halogen, acyloxy, hydroxyl, and alkoxy or mono-substituted by a cyano, acyl, phenyl or phenoxy group,

R_4, is a sulphur-free acyloxy or alkoxycarbonyl radical,

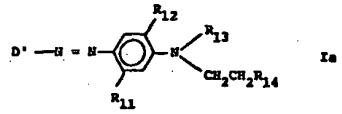
one of R_5 is R_5' is hydrogen and the other is methyl,

the D's R_1's R_2's and R_4's being identical, any alkyl groups or moieties and any alkoxy groups in such dyestuffs contain 1 to 8 carbon atoms, any alkenyl groups 2 to 4 carbon atoms, and said mixture contains 15 to 85% compound of formula I and 85 to 15% compound of formula II.

2. A mixture according to Claim 1, in which D is a radical of the benzene series, benzothiazolyl, thiazolyl or thiophene series.

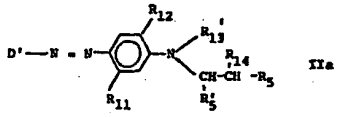
3. A mixture according to Claim 1 or Claim 2, in which D is thiophene-2-substituted by up to two nitro groups; benzothiazolyl-2 in which the benzene nucleus is substituted by up to two substituents selected from chlorine and nitro; or phenyl substituted in the para-position by nitro, alkylsulphonyl, aminosulphonyl, mono- or dialkyl-aminosulphonyl or phenylazo (which phenylazo is optionally substituted by up to three substituents selected from methyl, methoxy, chlorine, bromine and nitro) and optionally bearing up to two further substituents selected from halogen, nitro, cyano or alkylsulphonyl, any alkyl and alkoxy groups in said dyestuffs contain 1 to 4 carbon atoms.

4. A mixture according to any one of Claims 1 to 3, containing at least one compound of formula Ia



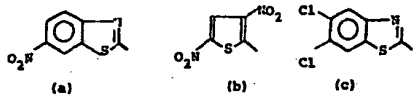
Ia

and at least one compound of formula IIa

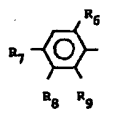


IIa

in which D' is a radical of formula (a), (b), (c) or (d)



(a) (b) (c)



(d)

wherein

R_6 is hydrogen, chlorine, bromine, iodine, nitro or cyano,

R_7 is nitro (C_{1-12})alkylsulphonyl, aminosulphonyl, mono- or di(C_{1-2})alkylaminosulphonyl or phenylazo in which the benzene ring is optionally substituted by up to three substituents selected from methyl methoxy, chlorine, bromine and nitro,

R_8 is hydrogen, chlorine or bromine,

R_9 is hydrogen, chlorine, bromine, iodine, cyano or (C_{1-2}) alkylsulphonyl, with the proviso that one of R_8 and R_9 is hydrogen,

R_{11} is hydrogen, methyl, methoxy, ethoxy, formylamino, alkyl (C_{1-4})carbonylamin , alkyl (C_{1-2})carbonylamino monosubstituted by hydroxyl, chlorine, bromine, cyano, phenyl, (C_{1-3})alk xy or phen xy, alkoxy-(C_{1-4})carbonylamin , th xycarbonylamin m n substitut d by hydroxy, (C_{1-3})alk xy or (C_{1-2}) alkoxyeth xy, benz ylamino r (C_{1-2})alkylsulphonylamino,

R_{12} is hydrog n, methyl (C_{1-2})alkoxy, (C_{1-2})-alk xyethoxy or (C_{1-2}) alkoxy monosubstituted by hlorine, bromin , cyano r phenyl,

R_{13} is hydrog n, linear (C_{1-4})alkyl, (C_{2-3})-alkenyl, linear (C_{2-3})alkyl mono-substitut d by (C_{1-2})alkoxy, cyano, formyloxy, alkyl (C_{1-4}) carbonyloxy, alk xy(C_{1-3})carbonyl, benz yloxy or alkoxy (C_{1-3})carbonyloxy,

R'_{13} has one of the significances of R_{13} but where the alkyl and substituted alkyl radicals are linear or branched,

R_{14} is formyloxy, alkyl (C_{1-4})carbonyloxy, benzoyloxy, phenoxyacetoxy, alkoxy (C_{1-4})-carbonyloxy, alkoxy(C_{1-4})carbonyl, alkoxy (C_{1-2}) ethoxycarbonyl, alkoxy (C_{1-2})ethoxycarbonyloxy, alkoxy-(C_{1-2})alkyl(C_{1-2}) carbonyloxy, mono- or di (C_{1-4}alkyl) aminocarbonyloxy or phenyl-aminocarbonyloxy wherein the benzene nucleus is optionally substituted by up to two substituents selected from chlorine, bromine, methyl and methoxy,

whereby in such mixture D', R_{11}, R_{12}, and R_{14} in the compound of formula Ia is identical with that of the compound of formula IIa.

5. A mixture according to Claim 4, in which D' is a group of formula (d).

6. A mixture according to Claim 4 or CLAIM 5, IN WHICH R_6 is R'_6, where R'_6 is hydrogen, chlorine, bromine or nitro, R_7 is nitro, R_8 is hydrogen and R_9 is R'_9 where R_9' is hydrogen, chlorine, bromine, cyano or methylsulphonyl.

7. A mixture according to any one of Claims 4 to 6, in which R_{11} is R'_{11}, where R'_{11} is hydrogen, methyl, alkyl (C_{1-2}) carbonylamino, chloro- or bromoalkyl-(C_{1-2}) carbonylamino, alkoxy (C_{1-2}) carbonylamino or alkoxy-(C_{1-2}) ethoxycarbonylamino, R_{12} is R'_{12}, where R'_{12}, where R'_{12} is hydrogen, methoxy or ethoxy, R_{13} is R_{13a}, wherein R_{13a} is linear (C_{2-3}) alkyl, allyl or linear (C_{2-3}) alkyl monosubstituted by cyano, alkyl (C_{1-2}) carbonyloxy, alkoxy (C_{1-2})-carbonyl or alkoxy (C_{1-2}) carbonyloxy, R'_{13} has one of the significances of R_{13a} but where the optionally substituted (C_{2-3}) alkyl may be linear or branched and R_{14} is alkyl-(C_{1-2}) carbonyloxy or alkoxy (C_{1-2}) carbonyloxy.

8. A mixture according to any one of Claims 1 to 6, in which R_5 is hydrogen and R'_5 is methyl, R_1 is R_{11} R_2 is R_{12}, R_3 is R_{13}, R'_3 is R'_{13} all as defined in Claim 4 and R_4 is acyloxy.

9. A mixture according to Claim 8, in which R_4 is alkyl (C_{1-2}) carbonyloxy or alkoxy (C_{1-2}) carbonyloxy.

10. A mixture according to Claim 8 or Claim 9 in which R_{11}, R_{12}, R_{13} and R'_{13} are as defined in Claim 7.

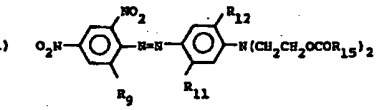
11. A mixture according to Claim 4, where D' is a radical (d) wherein R_6 is chlorine or bromine, R_7 is nitro, R_8, R_9, R_{11} and R_{12} are hydrogen, R_{13} and R'_{13} are cyanoethyl, R_{14} is alkyl (C_{1-2}) carbonyloxy, R_5 is methyl and R'_5 is hydrogen;

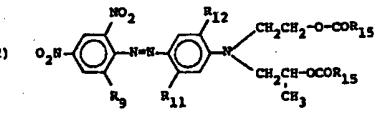
12. A mixture according to Claim 4, where D' is a radical (d) wherein R_6, R_8, R_{11} and R_{12} are hydrogen, R_7 is nitro, R_9 is cyano, R_{13} and R'_{13} are cyanoethyl, R_{14} is alkyl (C_{1-2}) carbonyloxy, R_5 is methyl and R_5' is hydrogen;

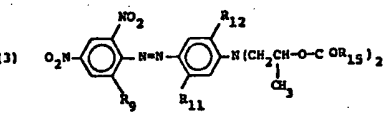
13. A mixture according to Claim 4, wherein D' is a radical (d) wherein R_6 and R_9, independently, are chlorine, or bromine,

R_7 is nitro, R_8, R_{11} and R_{12} are hydrogen, R_{13} and R'_{13} are cyanoethyl, R_{14} is alkyl (C_{1-2}) - carbonyloxy, R_5 is methyl and R'_5 is hydrogen;

14. A mixture according to Claim 4, comprising the following three dyestuffs

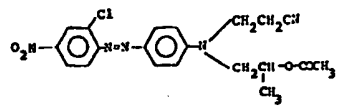
(1) 

(2) 

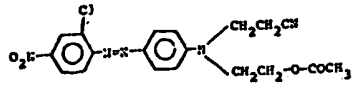
(3) 

in which each R_9 is chlorine, bromine or iodine, especially bromine, each R_{11} is alkyl (C_{1-2})-carbonylamino, each R_{12} is (C_{1-2}) alkoxy, and each R_{15} is (C_{1-2}) alkyl.

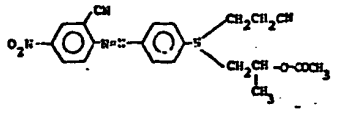
15. A mixture containing 15 to 85% dyestuff of formula



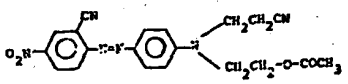
and 85% to 15% dyestuff of formula



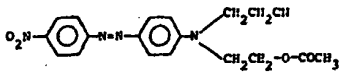
16. A mixture containing 15% to 85% dyestuff of formula



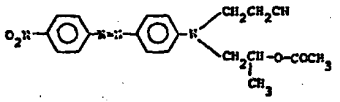
and 85 to 15% dyestuff of formula



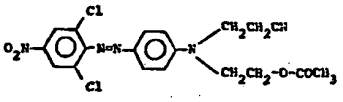
17. A mixture containing 15 to 85% dyestuff of formula



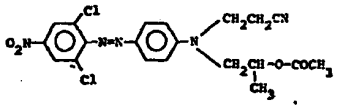
and 85 to 15% dyestuff of formula



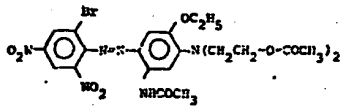
18. A mixture containing 15 to 85% dyestuff of formula



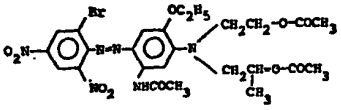
and 85 to 15% dyestuff of formula



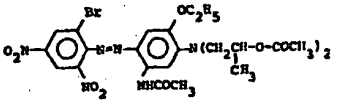
19. A mixture containing approximately 25% dyestuff of formula



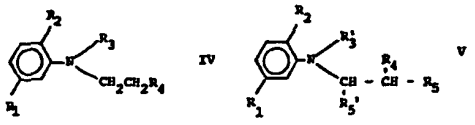
approximately 50% dyestuff of formula



and approximately 25% dyestuff of formula



20. A process for the preparation of a mixture according to Claim 1, comprising, coupling a diazotized amine with at least one compound of formula IV and at least one compound of formula V,



whereby at least 15 mol % f a compound of formula IV and at least 15 mol % of a compound of formula V is present.

21. A process for the preparation of a mixture according to Claim 1, substantially as hereinbefore described with reference to any one of Examples 1 to 57.

22. A mixture of disperse dyestuffs whenever obtained by a process according to Claim 20 or Claim 21.

23. A process for dyeing or printing synthetic or semi-synthetic, hydrophobic, high-molecular weight organic textile substrates from aqueous suspension comprising employing a mixture according to any one of Claim 1 to 19 or 22 as dyeing agent.

24. A process for dyeing or printing synthetic or semi-synthetic, hydrophobic, high-molecular weight organic textile substrates substantially as hereinbefore described with reference to any one of Examples A to C.

25. Dyed or printed substrates whenever obtained by a process according to Claim 23 or 24.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon Surrey, 1980.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.